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(54) Synthetic films with zeolite crystal bodies, and methods of making and using them.

(57) A synthetic film constituted of zeolite crystal body and alumina substrate; the alumina substrate containing more than 90wt% of alumina with pores having a mean diameter of 0.1-3.0μm and the zeolite crystal body is formed in the pores and on the substrate. Such synthetic film is manufactured by preparing the alumina substrate; immersing the substrate in a slurry containing zeolite crystal and its precursor prepared from a silica source using sodium silicate or water glass; and subjecting the substrate with a slurry to a hydrothermal crystallization one time or more.

EP 0 511 739 A1

The present invention relates to a synthetic film of zeolite crystal body for use e.g. in separating a useful component from a mixture, and a method for manufacturing the zeolite film. Preferred aims include the provision of a high separation efficiency due to ceramic pores, and also molecular sieving properties and properties as a catalyst of zeolite.

Conventional methods for separating a useful component from a mixture; namely a distillation process, a filtration process, and an adsorption process, etc. are well known. In the distillation, since the mixture should be heated up in order to separate the useful component therefrom, the method has a disadvantage in consuming energy. Further, the method has other disadvantages in that: the apparatus for performing the distillation method becomes large in scale; it is difficult to separate the useful components when the boiling point of the useful Component is close to those of other components; and the distillation cannot be applied to the mixture having a low vapour pressure and low heat resistance properties.

In the filtration method, there are also drawbacks namely that hydrocarbon polymer membrane cannot be put into wide use; a small molecular component cannot be separated from the mixture; and the filter per se does not have heat resistance properties and high strength. Further, in the adsorption and separating, the apparatus therefore becomes large in scale, and it is difficult to separate a highly concentrated useful component from the mixture, since the useful component is separated from the mixture with the add of equilibrium in adsorption.

The conventional methods mentioned in the above are mainly used for separating and refining reactants and products of reactions. Recently, a synthetic inorganic film comprising zeolite crystal held on a ceramic supporting body has been developed. Zeolite, aluminosilicate crystal, is widely used as powder in form for molecular-sieve, catalyst, etc. However, with this synthetic film, reaction of the mixture can be performed, and then the products successively separated. Such synthetic film is, for instance, disclosed in JP-A-61/107902, JP-A-1/148771 and JP-A-3/112808.

However, in these publications, there is no detail description concerning an optimum condition of the ceramic supporting body and zeolite held thereon, which constitutes the synthetic film, and the method for manufacturing such synthetic film having the optimum condition, Furthermore, according to the method disclosed in these publications, a highly densified film cannot be obtained. Therefore, not only can separating and refining not be performed successively in reaction of the mixture with such synthetic film, but also a synthetic film having a high strength cannot be obtained. Further, in the synthetic film, zeolite is held on a honeycomb-like ceramics substrate with pores having a mean diameter of several millimeters or more. The purpose for holding a zeolite on such a substrate is not to utilize the zeolite as a filter but to reduce the pressure loss. Thus it is not possible to separate the useful component from the mixture with the aid of pores having a mean diameter of smaller than ten Å, formed in the zeolite crystal.

The general problem addressed herein is to provide a novel zeolite synthetic film, and methods of manufacture and use thereof. In particular, it would be preferred to achieve a high strength, by which separation and refining of a useful component can be performed successively with high efficiency in reaction of a mixture containing the useful component.

A synthetiC film using zeolite crystal body according to the present invention comprises:

a porous substrate comprising at least 90wt% of alumina, diameters of the pores being generally about 0.1~3.0 μm; and

zeolite crystal body being formed in said pores of said substrate and on said substrate with a high density.

Further, a method for manufacturing synthetic film of zeolite crystal body according to the present invention comprises the following steps:

preparing a substrate with pores, whose diameters are about 0.1~3.0 μm, comprising more than 90 wt% of alumina;

immersing at least one surface of said substrate into a slurry comprising zeolite crystal body and a precursor thereof prepared from a silica source of e.g. silicate sodium or water glass; and

subjecting said substrate with slurry to a hydrothermal crystallization at least once.

In the present invention, the synthetic film of zeolite crystal body comprises a substrate with pores for supporting zeolite crystal body; the substrate has a given composition and pores therein having given diameters; and the zeolite crystal is formed in the pores and on the surface of said substrate with a high density. Therefore, the separation and refining of the useful component can be performed in the reaction of the mixture containing the useful component to be separated and refined; and further, the strength of the synthetic film becomes high. That is to say, since the interatomic distance of alumina is similar to that of zeolite crystal body, when alumina is used as a material of the ceramic substrate the alumina and the zeolite crystal body are strongly bonded to each other; as a result, the zeolite crystal body has less tendency to be exfoliated from the substrate.

When the purity of alumina in the substrate is less than about 90wt% and the impurity such as CaO is increased therein, the interatomic distance of a substance constituting the substrate becomes different from that of the zeolite crystal body, and then a bonding strength between the zeolite crystal body and the substrate becomes so weak that the synthetic film, whose substrate comprises less than about 90wt% of alumina and the impurities, could not to be put in a practical use. Further, since the crystal diameter of the zeolite crystal body obtained by the hydrothermal crystallization method according to the present invention is about zero point several micro meters to five micro meters, when the mean diameter of pores formed in the alumina substrate is less than about 0.1μm, almost no zeolite crystal body is formed in the pores, so that the zeolite crystal body could not be held on the alumina substrate more. On the other hand, when the mean diameter of pores exceeds about 3.0μm, zeolite crystal body can be formed in the pores but the inside of the pores are not filled with the zeolite crystal body with a high density, so that spaces would be generated in the pores and unevenness of the zeolite film would be formed on the surface of the substrate and then the efficiency of the synthetic film would be affected.

Furthermore, according to a method of the present invention, a synthetic film is manufactured by the steps of; preparing a substrate with pores, whose mean diameter is between 0.1~3.0 μm, comprising more than 90 wt% of alumina; immersing at least one surface of said substrate into a slurry comprising zeolite crystal body and a precursor thereof prepared from a silica source of silicate sodium or water glass; and subjecting said substrate with slurry to a hydrothermal crystallization at least once. Therefore, the zeolite crystal body can be strongly bonded in the pores formed in the alumina substrate and on the alumina substrate; and the strength of the thus obtained synthetic film becomes high.

The hydrothermal crystallization is preferably performed in such a manner that: the substrate with slurry is subjected to a temperature of 70~90°C for a duration of 15 minutes to twelve hours to obtain a synthetic film of A-type zeolite crystal body and the substrate with slurry is held in an autoclave at a temperature of 160~200°C for 24 to 72 hours to obtain a synthetic film of ZSM-5 zeolite crystal body.

Fig. 1 is in electron micrograph showing a structure of particles in a cross sectional area of a synthetic film of A-type zeolite crystals formed on the outer surface of a ceramic filter embodying the invention;

Fig. 2 is on electron micrograph showing a structure in a cross sectional area of a synthetic film of ZSM-5 zeolite crystals formed on the outer surface of a ceramic filter embodying the invention;

Fig. 3 is a schematic view illustrating an X ray diffraction pattern when an X ray is irradiated on an alumina filter without zeolite crystal film;

Fig. 4 is a schematic view depicting an X ray diffraction pattern when in X ray is irradiated on an A-type zeolite crystal film;

Fig. 5 is a schematic view indicating in X ray diffraction pattern when an X ray is irradiated on a ZSM-5 zeolite crystal film;

Fig. 6 is a schematic view representing an X ray diffractien pattern when an X ray is irradiated on a synthetic film of A-type zeolite crystal body formed on the outer surface of the ceramic filter;

Fig. 7 is a schematic view showing an X ray diffraction pattern when an X ray is irradiated on a synthetic film of a ZSM-5 zeolite crystal body formed on an alumina substrate; and

Fig. 8 is a schematic view illustrating a cell for separating oxygen from air in which a synthetic film of zeolite crystal body embodying the invention is used.

Fig. 1 is an electron micrograph showing a cross sectional structure of a synthetic film of A zeolite crystal body embodying to the present invention; and Fig. 2 is an electron micrograph indicating a cross sectional structure of a synthetic film of ZSM-5 zeolite crystal body embodying the invention. The fact that a highly densified zeolite film is formed in pores of the alumina substrate and on the outer surface of the substrate is clearly observed in Figs. 1 and 2.

Figs. 3, 4 and 5 are schematic views representing X ray diffraction patterns when an X ray is irradiated on the alumina filter per se, A zeolite crystal body per se, and ZSM-5 zeolite crystal body per se, respectively; and Fig. 6 and 7 are schematic views illustrating X ray diffraction patterns when an X ray is irradiated on synthetic films of A zeolite crystal body and of ZSM-5 zeolite crystal body, respectively, which are formed on the alumina filter substrates.

Known as Y-type zeolite A-type zeolite or ZSM-5 zeolite, which are made of crystals of aluminosilicate, is preferably used to obtain the zeolite crystal body. It should be noted that these types of zeolite have a heat resistance against a temperature of 700°C. By the synthetic film according to the present invention, a separation of a useful component contained in a mixture containing the useful component and a reaction of the mixture with the zeolite are effected at the same time, when the mixture is passed through the pores formed in the alumina substrate and the zeolite crystal body formed in the pores and on the outer surface of the substrate.

Fig. 8 is a perspective view of a cell for separating oxygen from air in which a synthetic film embodying

the invention is applied. As shown in Fig. 8, the cell 4 comprises three nested cylindrical alumina tubes 2-1, 2-2, 2-3; on the surface of the outer large-size alumina tube 2-1 is formed a synthetic film of 5A zeolite crystal body, on the surface of the intermediate middle-size alumina tube 2-2 a synthetic film of 4A zeolite crystal body, and on the surface of the inner small-size alumina tube 2-3 a synthetic film of 3A zeolite crystal body, respectively. When air is introduced on the surface of the large-size alumina tube 2-1 at a high pressure, oxygen contained in the air is diffused into the films of the tubes 2-1, 2-2, 2-3, successively in this order. The oxygen becomes pure more and more during when the oxygen is diffused into the tubes, so that oxygen having a high purity can be continuously obtained from the inside of the inner alumina tube 2-3.

Further, a synthetic film embodying the present invention may be applied to separate and refine an isomer from butene isomer, whose chemical properties and boiling points are very similar. In this case, the isomer can be separated and refined from butene isomer without using a large reaction vessel and a distillation column.

A synthetic film embodying the present invention may also be applied to a sensor for detecting a substance only having a small minimum molecular diameter which can be diffused into the zeolite crystal body film. Such sensor comprises a cylindrical alumina tube, inside which is provided a sensor element for detecting a reducing material and outside which is arranged a synthetic film of zeolite crystals body having a molecular sieving effect. Such a sensor may be utilized, for instance, to detect an n-paraffin from a mixture of isoparaffin and n-paraffin. It should be noted that the chemical properties of n-paraffin and isoparaffin are very close to each other and thus it wag very difficult to discriminate them, hitherto.

One embodiment of a method for manufacturing a synthetic film of zeolite crystal body will be explained in the following.

An alumina substrate, in which a mean diameter of pores is about 1~2 μm and a purity is 99.9%; was prepared and the substrate was processed to obtain plate-like substrates of 30×30×3 mm or cylindrical substrates having their outer diameter of about 10 mm, thickness 2~3 mm and length 100 mm. To obtain several types of synthetic films on the substrates, zeolite crystals and and its precursor are prepared from a mixture of a liquid of sodium silicate powder or water glass, aluminum sulfate or aluminum hydroxide, NaCl and water; the thus obtained crystals and precursor are applied on the alumina substrates and then put it in an autoclave of 300~500 cc; in the autoclave, the alumina substrate with zeolite crystals and precursor were subjected to a hydrothermal crystallization in order to synthesize a zeolite film in the pores of the alumina substrate and on the outer surface of the alumina substrate. It should be noted that in order to synthesize a film of ZSM-5 zeolite crystal body, a template should be contained in the mixture liquid. The temperatures and hours of the hydrothermal Crystallization were set up as shown in the following Table to obtain synthetic films, some embodying and some not embodying the present concepts. In some of the examples in the Table, the hydrothermal crystallization was repeated several times. Further, in some of the examples, a silica gel was applied on the surface of the zeolite film and then sintered in air at a temperature of 500 °C to form a porous silica gel film on the zeolite film in order to increase the proof-abrasion characteristic of the zeolite crystal body.

Table 1

		Type of zeolite shape of substrate Diameter of pores	Hydrothermal crystallization condition		Number of times of hydrothermal crystallization	Density of zeolite film
			temperature	time		
Example	1	ZSM-5 plate 1 ~ 2 μm	normal temp. → 200°C 200°C Keep	24 Hr 72 Hr	1	good
	2	ZSM-5 cylindrical 1 ~ 2 μm	normal temp. → 200°C 200°C Keep	24 Hr 72 Hr	1	good
	3	ZSM-5 cylindrical 1 ~ 2 μm	normal temp. → 200°C 200°C Keep	24 Hr 48 Hr	1	good
	4	ZSM-5 cylindrical 1 ~ 2 μm	normal temp. → 200°C 200°C Keep	24 Hr 48 Hr	2	excellent
	5	ZSM-5 cylindrical 1 ~ 2 μm	normal temp. → 200°C 200°C Keep	24 Hr 48 Hr	3	excellent
	6	ZSM-5 cylindrical 1 ~ 2 μm	normal temp. → 200°C 200°C Keep	24 Hr 48 Hr	4	excellent
	7	A cylindrical 1 ~ 2 μm	normal temp. → 80°C 80°C Keep	3 Hr 9 Hr	1	good
	8	A cylindrical 1 ~ 2 μm	normal temp. → 80°C 80°C Keep	15 min. 12 Hr	1	good
	9	A cylindrical 1 ~ 2 μm	normal temp. → 90°C 90°C Keep	15 min. 6 Hr	1	good
	10	A cylindrical 1 ~ 2 μm	normal temp. → 90°C 90°C Keep	15 min. 6 Hr	2	excellent
	11	A cylindrical 1 ~ 2 μm	normal temp. → 90°C 90°C Keep	15 min. 6 Hr	3	excellent
	12	A cylindrical 1 ~ 2 μm	normal temp. → 90°C 90°C Keep	15 min. 6 Hr	4	excellent
Comparative example	1	ZSM-5 plate 3 ~ 5 μm	normal temp. → 200°C 200°C Keep	24 Hr 72 Hr	1	bad
	2	ZSM-5 cylindrical 3 ~ 5 μm	normal temp. → 200°C 200°C Keep	24 Hr 72 Hr	1	bad
	3	ZSM-5 ZrO_2 substrate cylindrical 1 ~ 5 μm	normal temp. → 200°C 200°C Keep	24 Hr 72 Hr	1	bad
	4	ZSM-5 MgO substrate cylindrical 1 ~ 5 μm	normal temp. → 200°C 200°C Keep	24 Hr 72 Hr	1	bad

As clear from Table, when the hydrothermal crystallization was conducted at a temperature and a time period as recommended herein, a synthetic film having good characteristics could be obtained, in comparison with the comparative examples of the synthetic films which were manufactured under non-preferred hydrothermal crystallization conditions.

The present invention is not limited to the above mentioned embodiments, but many modifications and alterations can be applied. For instance, in the embodiment, the alumina substrate having its purity of 99.9% is used to manufacture the synthetic film, but the other alumina substrate having a lower purity can be used so far as the mean diameter of the alumina substrate is in the scope of the present invention.

In the present invention, the synthetic film is obtained in such a manner that zeolite crystal body is formed on an alumina substrate having a given composition with the aid of hydrothermal crystallization. Therefore, the zeolite crystal body is bonded to the substrate with a high bonding strength; and therefore,

the useful component to be separated from the mixture can be separated and refined with a high efficiency at the same time of the reaction of the mixture; further, a synthetic film of a zeolite crystal body having a high strength, can be obtained.

Claims

1. A synthetic film of zeolite crystal body comprising:
   a porous substrate comprising more than 90wt% of alumina, diameters of the pores being about 0.1-3.0μm; and
   zeolite crystal body being formed in said pores of said substrate and on said substrate with a high density.

2. A synthetic film using zeolite crystal body according to claim 1, wherein:
   said zeolite crystal body is made of Y-type zeolite, A-type zeolite or ZSM-5 zeolite.

3. A synthetic film according to claim 1 or claim 2, wherein:
   a silica gel film is arranged on said crystal body.

4. A method for manufacturing a synthetic film of zeolite crystal body, comprising the following steps of:
   preparing a substrate with pores, whose diameters are about 0.1-3.0μm, comprising more than 90wt% of alumina;
   immersing at least one surface of said substrate into a slurry comprising zeolite crystal body and a precursor thereof prepared from a silica source of silicate sodium or water glass; and
   subjecting said substrate with slurry to a hydrothermal crystallization at least once.

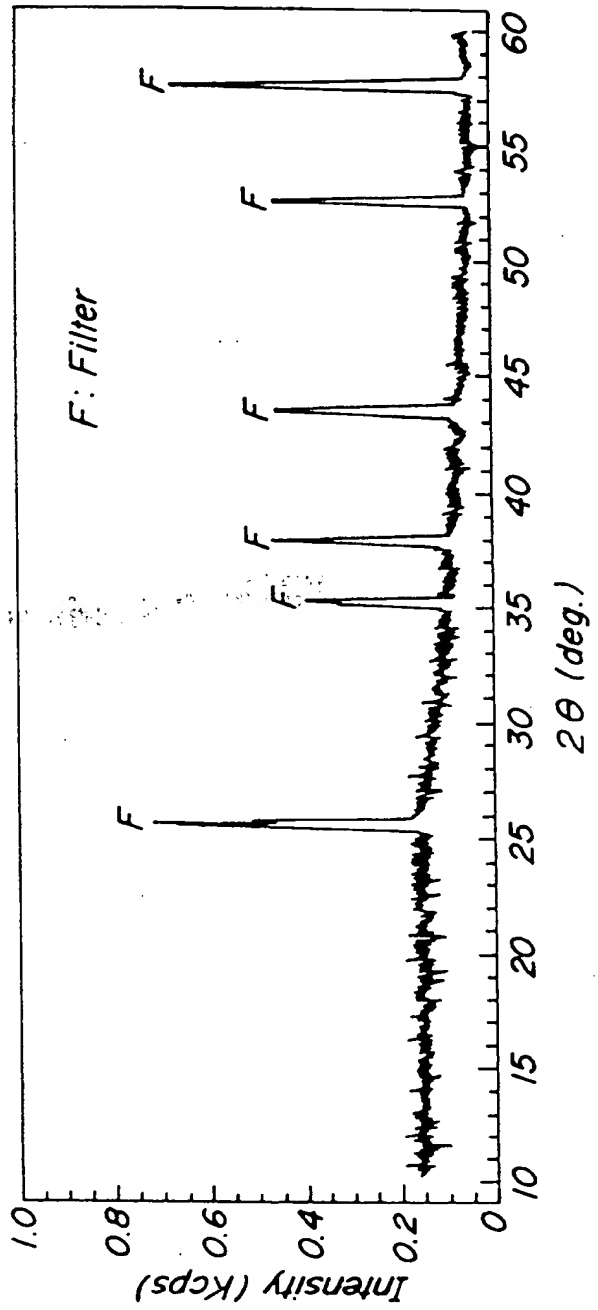
5. A synthetic film obtainable by the method of claim 4.

6. Use of a synthetic film, according to any one of claims 1 to 3, as a separating or sensing element.

FIG_1

FIG_2

FIG.3


F: Filter
F
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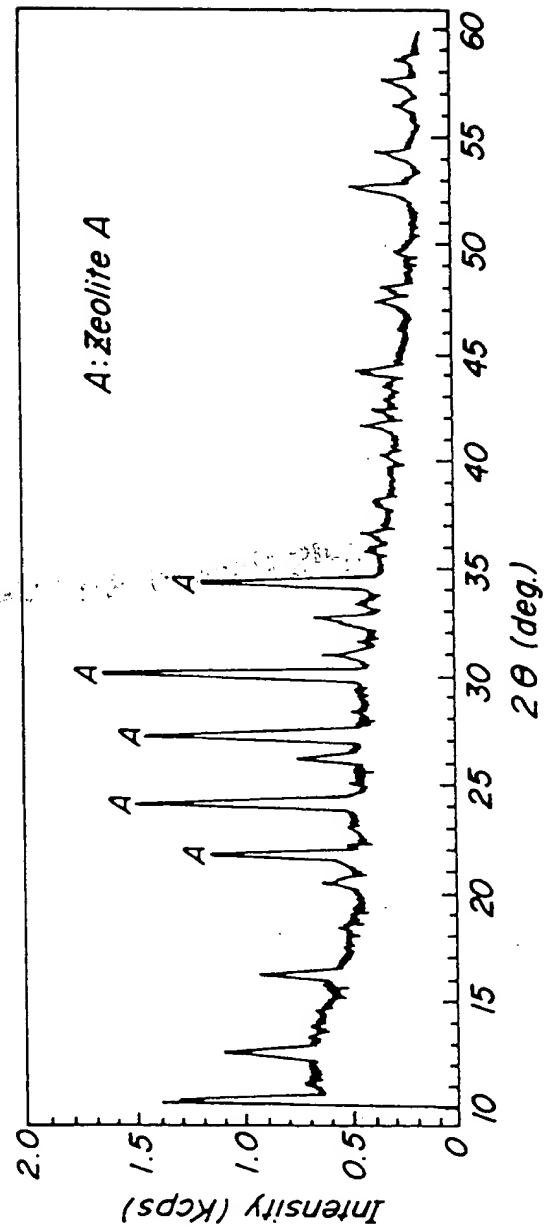
0.8
0.6
0.4
0.2
0
10
15
20
25
30
35
40
45
50
55
60
2θ (deg.)

FIG. 4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A
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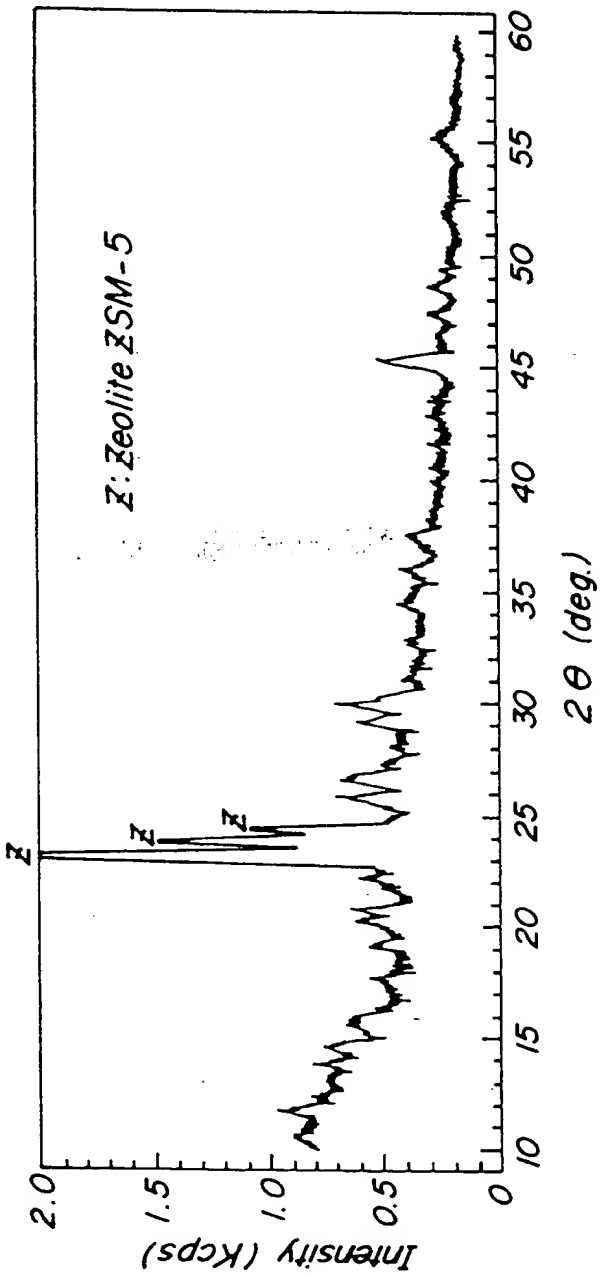
55
60
2θ (deg.)

FIG_5


Z: Zeolite ZSM-5
Z
Z
Z
Z
Intensity (Kcps)
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1.0
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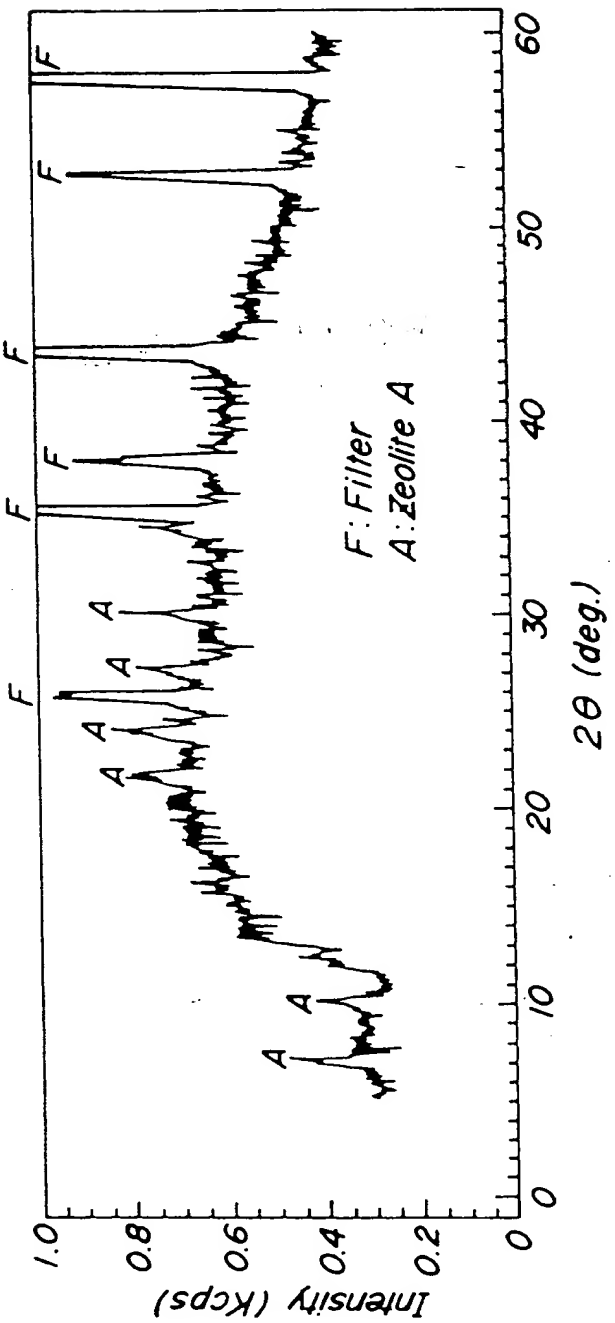
0
10
15
20
25
30
35
40
45
50
55
60
2θ (deg.)

FIG_6


Intensity (Kcps)
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0.4
0.2
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10
20
30
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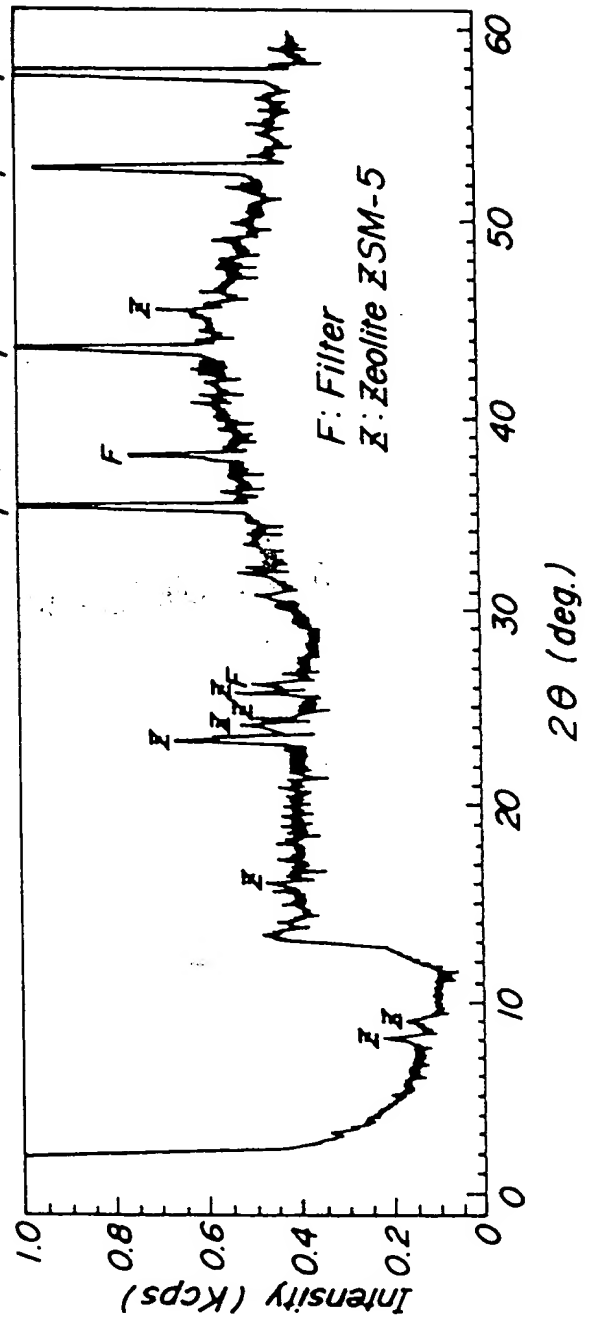
60
2θ (deg.)
F: Filter
A: Zeolite A
F
A

FIG_7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Z: Zeolite ZSM-5
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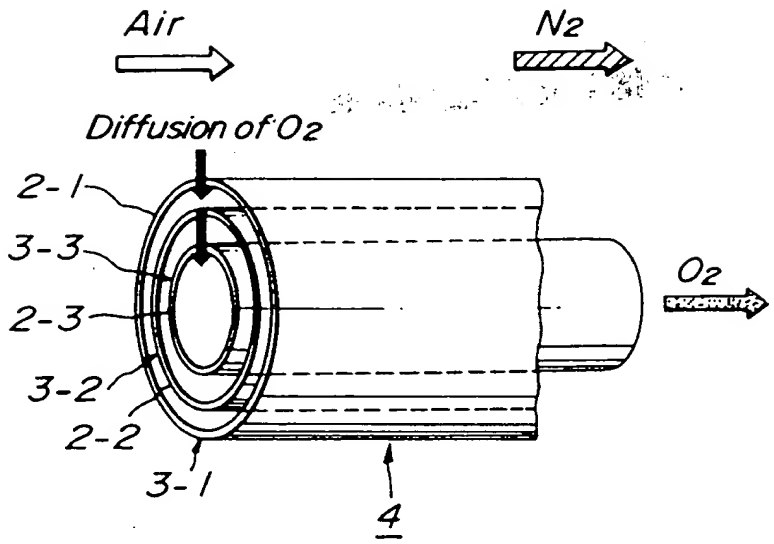
0.8
1.0
10
20
30
40
50
60

FIG_8



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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 2783

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	DE-A-3 827 049 (R. SCHULTEN) ASPECIALLY PAGE 3, EXAMPLE 1	1	B01D71/02
A	US-A-3 244 643 (A. B. SCHWARTZ) SEE COLUMN 2, LINES 3-49;	1	
A,P	EP-A-0 428 052 (AIR PRODUCTS AND CHIMICALS, INC.) ASPECIALLY CLAIMS 17,24,25	1	
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 119 (C-579)(3467) 23 March 1989 & JP-A-63 291 809 (IDEMITSU KOSAN CO LTD) 29 November 1988 * abstract *	1	
A	US-A-3 730 910 (E. W. ALBERS ET AL.)		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

B01D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	02 JULY 1992	DEVISME F. R.

CATEGORY OF CITED DOCUMENTS

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